Fabrication and application studies on surface-modified metal oxides nano-hetero-structured thin film electrodes in photoelectrochemical water splitting

Synopsis

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1. Energy – A pivotal force to sustain growth and development

Modern growth and development of societies rests critically on easy availability of energy at affordable cost. From the early use of animal power and fire that enhanced our life-quality, we have reached to the present state, where electricity has occupied the central place by being the most popular medium of energy and enabler of development. In this journey, fossil fuels have played a dominant role and continue to be a key regulator controlling the development and progress of countries. However, in the last few decades, the exponential rise in the combustion of fossil fuels (coal and oil), to meet the growing energy needs of the world, has also resulted in the atmospheric concentration of greenhouse gases going alarmingly high. The reported rise in the Earth's temperature by over one degree since the pre-industrial era is being seen as a serious threat to the survival of mankind on this planet. Additionally, the fossil fuel stock on Earth is also limited and is depleting fast, which is another cause of concern. In order to put a halt on global rise in temperature (expected to be more than two degrees by the end of this century), our overdependence on fossil fuels for energy supply to the society has to stop (pib.gov.in). To that effect, non-polluting and renewable alternate energy forms, like solar energy, have become tremendously significant, and must be tapped to address the growing challenges of global warming and climate change.

Like many other countries of the world, India has also geared up for energy transition and climate action, with the Government providing a roadmap for clean energy and mitigation of adverse climatic changes. This roadmap outlines certain commitments that need to be fulfilled by the end of the year 2030. These include: (i) increasing non-fossil energy capacity to 500 GW, (ii) fulfilling 50% of energy requirements from renewable sources and, (iii) reducing carbon emissions by one billion tonnes (pib.gov.in). The estimated total potential for renewable power generation in the country (as on March 2022) is 14,90,727 MW, which includes 7,48,990 MW (50.24%) solar power; 6,95,509 MW (46.66%) wind power; 21,134 MW (1.42%) small-hydro power; 17,538 MW (1.18%) biomass power; 5,000 MW (0.34%) power from bagasse-based cogeneration in sugar mills; and 2,556 MW (0.17%) power from wastes (https://www.mospi.gov.in). The continued transition from fossil fuels to renewable energy is accompanied by a diversification of energy conversion technologies such as hydropower (including tidal and wave power), geothermal, biomass-derived power (biomass, biogas,

biofuel), wind power, and solar energy focusing on concentrated solar power (CSP) (Mollmann et al; 2020). It is also very obvious that for a country like India, where in many areas and for most part of the year solar radiation intensity on Earth's surface is very high, solar energy is the most viable renewable energy option. Still, this intermittently available solar energy (bound by the diurnal cycle) needs to be captured and stored in a form, from where it can be made easily available for use in different sectors of the society. In this context, Hydrogen has emerged in recent years as a promising alternate fuel (energy carrier), which is non-polluting and reliable. Solar energy can be captured and stored in the form of hydrogen by photosplitting of water. Later, while using this hydrogen as fuel; its burning in air/oxygen would complete the cycle of material flow, yielding the stored energy as heat and regenerating water as by-product.

Solar energy flux reaching the Earth's surface is dominated by visible component, with small percentages of ultraviolet and infrared components. Since, water is transparent in the visible portion of light, a suitable photocatalyst/photosensitizer is needed to absorb this visible component of solar light efficiently and transfer the absorbed energy to water molecule for its dissociation into hydrogen and oxygen. The thermodynamic Gibbs free energy required for the dissociation of water molecule is ≈ 1.23 eV. Further, in a real-time water-electrolysis set-up, several energy losses viz. polarization-induced overvoltage etc. are also encountered. Hence, the actual energy required for dissociation of water molecule is 1.8-2.0 eV. While this required energy is fed solely as electricity in the normal electrolysis of water; in a photoelectrochemical cell device, it is either partly or fully provided as light. There are many semiconductors (metal oxides being the most promising) with a band gap energy falling in this range and can be suitable candidates for this application.

2. Photoelectrochemical cell: A viable technology for renewable hydrogen generation

The photoelectrochemical (PEC) approach to generate renewable hydrogen by photo-splitting of water has drawn the attention of many researchers world over in last few decades. Due to its relatively high theoretical efficiency (30.7%), this technological approach is being perceived as one of the green channels for renewable hydrogen fuel generation on a sustainable basis (Aslam et al; 2024). PEC cell system works on the principle, where solar energy is absorbed by a suitable semiconductor and the resulting electrons and holes then participate, respectively at cathode and anode in hydrogen and

oxygen evolution redox processes (Zhou et al; 2020). Compared to the conventional electricity-fed water electrolysis systems, in PEC cell the energy needed to dissociate water molecule is provided (in part or full) by the photoenergy, which would be ultimately the solar light energy. The single step conversion of solar light energy to hydrogen in PEC cell promises this technology to be more efficient than the photovoltaic cell coupled with electrolyser. The Photoelectrochemical technology is the most promising option also because it involves solar energy and water, both of which are abundantly available on Earth's surface. Moreover, it is comparatively uncomplicated which makes it an attractive technique for diverse applications. It is also worth mentioning that the PEC technology is not only valuable for water splitting to generate renewable Hydrogen fuel, but holds significance for diverse other applications like, optical sensing, carbon dioxide reduction, and remediation of recalcitrant organic pollutants (Rani et al; 2024).

3. PEC water splitting: Reaction pathways

PEC water splitting is an ideal technology to split water into hydrogen and oxygen and is analogous to "Artificial Photosynthesis" in which photon energy is converted into chemical energy (i.e. high-energy chemical compounds). In this canonical model, a light-sensitive semiconductor photoelectrode is immersed in an aqueous solution, with electrical wiring connected to a metallic counter (auxiliary) electrode. With the illumination of sunlight, photogenerated electron-hole pairs in the semiconductor interact electrochemically with ionic species in solution at the solid/liquid interfaces (Bak et al., 2002). With regard to the photosplitting of water following sequence of reactions occur in this process when an n-type semiconductor is used as photoanode.

Step 1: Absorption of light by semiconductor photoelectrode generates electron (e^-) and hole (h^+).

$$2h\nu \rightarrow 2e^- + 2h^+ \quad \text{(i)}$$

Step 2: Electrons (majority charge carriers in this case) are migrated to the metal counter electrode (typically the platinum electrode), where they participate in the reduction of water to evolve hydrogen, as shown below.

$$2e^- + 2H_2O \rightarrow H_2\,(g) + 2OH^- \quad \text{(ii)}$$

Step 3: Holes (minority charge carriers in this case) drift to the surface of the semiconductor photoanode, where they participate in the oxidation process and produce oxygen.

$$2h^+ + 2OH^- \rightarrow \tfrac{1}{2}O_2\,(g) + H_2O \qquad \text{(iii)}$$

Step 4: Transport of OH^- from cathodic to anodic compartment through the electrolyte completes the electrochemical circuit. The overall reaction may be written as,

$$2hv + H_2O \rightarrow H_2\,(g) + \tfrac{1}{2}O_2\,(g) \qquad \text{(iv)}$$

In PEC cell, electrodes can be arranged in different ways. Few possible arrangements are as follows: (i) Photoanode: n-type semiconductor, Cathode: p-type metal; (ii) Photocathode: p-type semiconductor, Anode: n-type metal; (iii) Photocathode: p-type semiconductor, Photoanode: n-type semiconductor.

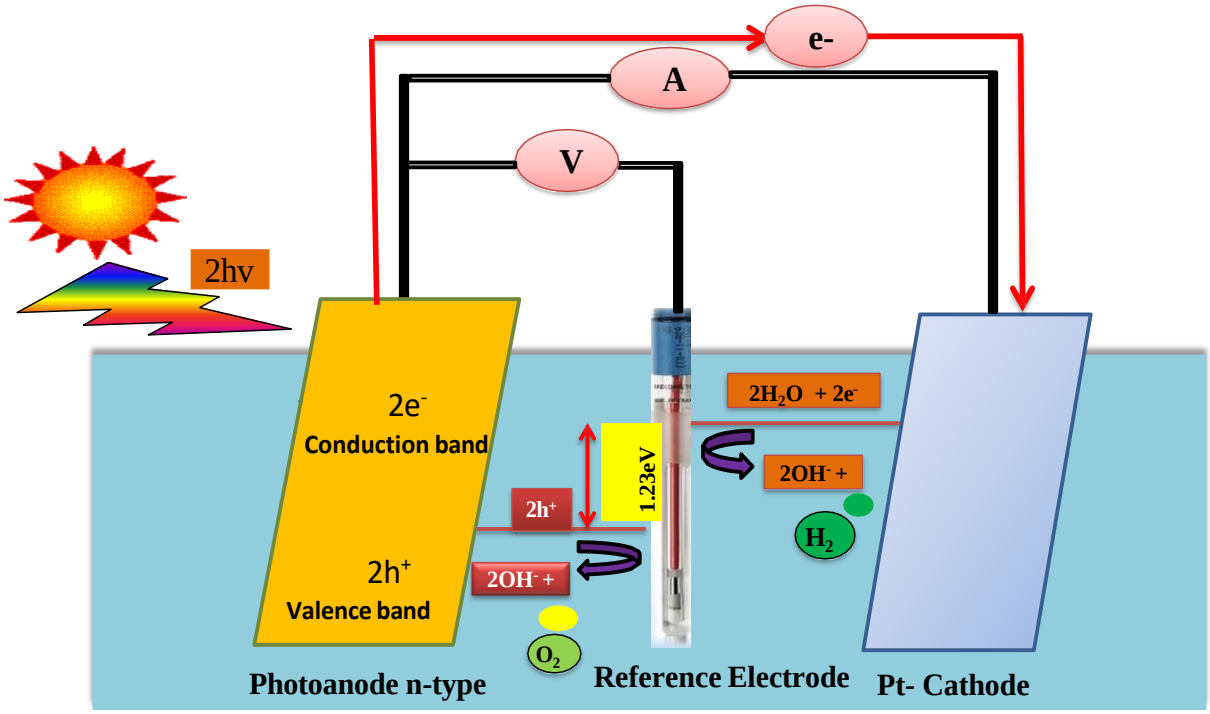

Fig 1: Schematic arrangements and reaction pathways for water splitting in a typical PEC cell.

4. Metal oxides: Most attractive class of materials for PEC applications

Among the different prospective semiconductor materials for application in PEC cell, metal oxides are attractive due to their high stability, low-cost, and excellent compositional and structural flexibility. Furthermore, the adjustable bulk and surface components in metal oxides offer great potential to tune their properties for efficient photo-excitation and PEC water splitting. Table 1 below lists few identified metal oxides, along with their important properties, which would remain of interest in the proposed study.

Table 1: Few prospective metal oxide semiconductors for PEC splitting of water

Semiconductor	Bandgap (VB edge, CB edge) (eV)	Properties
WO_3	2.6 (3.1, 0.5)	• Material with n-type conductivity. • Earth-abundant, non-toxic, high water oxidation activity. • Stable in many phases, including monoclinic, orthorhombic, hexagonal, and cubic, with several hydrated crystalline phases of different stoichiometry. • Stable over a wide range of pH. *Limitations* • Sluggish catalytic kinetics and undesired photo-corrosion in highly acidic/alkaline electrolyte solutions during the photo-assisted oxygen evolution reaction (OER).
$ZnBi_2O_4$	2.87 (2.93, 0.06)	• Shows both p & n type conductivity. • Single phase crystal with tetragonal symmetry. • Chemically stable in electrolyte, strong • oxidizing power, and highest photoluminescence emission at 600 nm. *Limitations* • Wide band gap, fast recombination, photo corrosive, sluggish electrochemical properties.
$MnTiO_3$	3.1 (2.64, -0.46)	• Rhombohedral pyrophanite phase. • Band edges straddle with redox potential of water. • n-type of conductivity. • High photocorrosion resistance. • Highest photoluminescence emission at 450 nm. *Limitations* • Incomplete visible light harvesting (absorbs in UV region).
$BiVO_4$	2.4 (2.86, 0.46)	• Stable in aqueous electrolyte and nontoxic. • Direct band gap material. • n-type conductivity. *Limitations* • Dominance of water oxidation reaction.
TiO_2	3.2 (2.95, -0.25)	• Suitably aligned band edges. • Chemically stable. • Low cost material. • n-type conductivity *Limitations* • UV absorber, wide band gap, fast recombination.
Co_3O_4	2.07 (2.37, 0.30)	• p-type conductivity. • High catalytic behaviour for water splitting. • Highly stable in aqueous alkaline environment. *Limitations* • Slow separation of photo-induced electron-

		hole pairs.
$NiWO_4$	2.6 (3.2, 0.6)	• Indirect bandgap of 2.6 eV. • n-type conductivity. • Remarkable quantum size effect makes it a potential photoanode candidate for H_2O splitting. • Wolframite-type monoclinic structure. • Low cost material with good photocatalytic activity in both neutral and alkaline medium. *Limitations* • Sluggish hole-transfer with faster recombination. • Slow charge mobility.
ZnO	3.2 (3.35, 0.15)	• n-type material with direct band gap. • With high photosensitivity, photochemically stable it is a low cost material which has strong oxidizing power. • Large exciton binding energy of 60 meV. *Limitations* • Wide band gap, fast recombination and low quantum efficiency. • Incomplete visible light harvesting and photocorrosion.

5. Fabrication of suitable semiconductor photo electrode: Emerging opportunities

Semiconductor photo electrode which is undoubtedly the most important component of PEC cell, plays a vital role in hydrogen evolution. The lifetime of photo evolved charge carriers (e^- and h^+) ranges in picoseconds, which makes it very challenging to eliminate/reduce their recombination for hydrogen/oxygen evolution reactions to proceed efficiently. Thus, the selection of suitable material (semiconductor) is most critical, as it should simultaneously meet multiple requirements of efficient light absorption, high stability, long life time with swift migration of charge carriers, and of being low-cost with easy availability. As satisfying all these requirements there is no semiconductor identified till now, researchers are investigating to tailor the material properties through different modification strategies viz. impurity doping, swift heavy ion irradiation, ion implantation, and combination of materials with the growth of nano-hetero-structures. It has also been observed that the variation in material preparation method and the preparation conditions significantly alter even the microstructural properties of the material formed, which imparts in many cases critical influence on the PEC performance of such materials. Incorporating a dopant (metal or non-metal) not only alters the electronic structure but also introduces a local built-in electric field, which facilitates the charge

mobility and separation of photo generated electron-holes (Xin et al; 2020). Obregon and Colón (2014) synthesized Er^{3+} doped $BiVO_4$ with the exceptional photo degradation ability for dye degradation and oxygen evolution. With regard to the fabrication of efficient semiconductor photo electrode, among different ways to tailor the properties, nano-hetero-structuring has aroused much interest in recent years. The bilayered nano-hetero-structured PEC devices, formed with the combination of low and high bandgap materials, are expected to offer synergistic effect on light absorption, enabling absorption of much larger spectrum of solar-light. Besides, such systems with properly aligned band edge structure at the junction may also facilitate the charge separation, resulting in reduced recombination losses (Choudhary et al., 2012). Both the above effects are expected to enhance the photoconversion efficiency (Kale et al., 2009). Bilayered nano-hetero-structuring is reported to alter even the crystal structure in few cases. The Er^{3+} doped $BiVO_4$ prefers to be tetragonal phase instead of monoclinic phase due to the formation of tetragonal $ErVO_4$ seeds previous to $BiVO_4$ formation.

6. Proposed Study and Objectives

Proposed plan of work aims to fabricate surface-modified nano-hetero-structured thin film photoelectrodes of identified metal oxides semiconductors (Table 1), which will be thoroughly characterized and tested for their performance in PEC splitting of water. While designing and fabricating bilayered nano-hetero-structured thin film photoelectrodes, proposed investigations would involve combining only a suitable pair of materials (from a relatively longer list given in Table 1), having suitably aligned band edge characteristics at the interface (preferably a staggered type arrangement) for PEC water splitting. The planned surface modifications include (i) impurity incorporation in varied amounts, (ii) regulated embedding (decorating) of the deposited film layers with biologically/chemically derived metal nanoparticles, and (iii) controlled chemical etching of the deposited films. The main objectives/stages of the proposed work are listed below:

- To synthesize layered thin film nano-hetero-structures of identified metal oxide semiconductors by wet chemical routes, viz. sol-gel spin coating/spray pyrolysis.
- To induce surface modifications via during- and/or post-growth treatment of the prepared thin films.

- ❖ To characterize prepared film samples for crystallographic, microstructural, morphological, topographical and optical properties, relevant for their application as photoelectrode in PEC splitting of water.
- ❖ To observe and evaluate critically the fabricated thin film electrodes for their performance and stability in PEC splitting of water.

7. Proposed Methodology

Thin films of metal oxide semiconductors will be grown over pre-cleaned conducting glass substrates (ITO plates) by a wet chemical methods (sol-gel spin coating and spray pyrolysis). After deposition, films will be sintered in air at elevated temperatures to allow the desired crystalline phases to evolve and expand. Different approaches (as outlined in Table 2) would be followed to induce during- and/or post-growth surface modifications in films. Thus obtained thin films would be thoroughly characterized for: (i) crystallographic and microstructural characteristics by X-ray diffractometry (XRD) and Transmission Electron Microscopy (TEM), (ii) optical characteristics by UV–Visible spectrometry, (iii) surface morphology and topography by Field Emission – Scanning Electron Microscopy (FE-SEM) and Atomic Force Microscopy (AFM), and (iv) elemental composition by Energy Dispersive X-ray analysis (EDX) and X-ray photoelectron spectroscopy (XPS). Synthesized thin films would then be fabricated as photoelectrode and tested for their performance in a three-electrode photoelectrochemical cell, in conjunction with platinum counter electrode and saturated calomel reference electrode, for splitting of water. PEC measurements would involve recording the current (I) – voltage (V) characteristic plots of the PEC cell both under darkness and illumination, from which the photocurrent values and the conversion efficiencies would be evaluated.

8. Key work-elements and study-parameters

Key work-elements and different parameters of investigation in the proposed work-plan have been outlined in Table 2.

Table 2: Key work-elements

Parameters of the study	Description
Preparation of samples Designing and fabrication of bilayered nano-hetero-structured thin film electrodes of material-pairs having suitably aligned band edge characteristics at the interface (preferably a	• Metal oxides of interest would be: TiO_2, ZnO, WO_3, Co_3O_4, $BiVO_4$, $ZnBi_2O_4$, $MnTiO_3$, $NiWO_4$

staggered type arrangement) for PEC water splitting.	
Proposed strategy for film-growth	• Bi-layered nano-hetero-structures grown as ITO supported thin film with surface modifications induced by: (i) Impurity incorporation (metallic/non-metallic) in varied amounts. (ii) Regulated embedding (decorating) of the deposited film layers with biologically/chemically derived metal nanoparticles. (iii) A controlled chemical etching of the deposited films.
Proposed method for the preparation of samples	Wet chemical methods (sol-gel spin coating deposition and spray pyrolysis).
Expected variables in the study	• Nature of metal oxides and their combination in nano-hetero-structures. • Sintering temperature and conditions of film growth. • Nature and doses of impurity incorporated. • Nature and doses of surface embedded metal nanoparticles. • Nature and concentration of etching reagent and the contact duration.
Characterization	Crystallographic, microstructural, morphological, topographical and optical properties, relevant for use of prepared thin films as photoelectrode in PEC splitting of water.
PEC measurement variables	• Current (I) – Voltage (V) characteristics of PEC cell under darkness and illumination. • Photocurrent • Open circuit potential (V_{oc}) • Short circuit current (I_{sc}) • Onset voltage • Applied bias photon to current conversion efficiency (ABPE)

9. Importance of the proposed work

It is very much obvious now that, renewable hydrogen generation through solar-light mediated splitting of water is a promising approach to meet the energy needs of the world on a sustained basis. From the literature survey it is also apparent that, the photoelectrochemical route of water dissociation holds much superiority over many other methods. Still a concerted effort is needed, both in fundamental research and the development of technology to exploit the decisive potential of PEC water splitting in commercial generation of renewable hydrogen. The proposed plan of work lies within the ambit of fundamental research. It is focussed on the fabrication of nano-hetero-structured thin film photoelectrodes of identified metal oxide semiconductors, along with induced surface

modifications to explore their performance in photoelectrochemical splitting of water. By delving into this still scantily studied territory, the study is expected to generate crucial understanding on the role and effects of different surface modifications in incrementing the performance of such nano-hetero-structures of metal oxides, towards PEC splitting of water.

Annexure 1

Current Status of Knowledge: Highlights of Recent Research Reports

A summarized presentation of few recent investigations by different researchers on metal oxides having desired band gap and efficient optical properties for PEC water splitting is given below:

Li et al (2024) have successfully synthesized p-type copper niobate ($CuNb_2O_6$) thin films using a two-step spray pyrolysis method on FTO glass substrates. X-ray diffraction (XRD) analysis has confirmed the high phase purity of the ($CuNb_2O_6$) films, with the intensity of the main peak increasing with annealing temperature, indicating enhanced crystallization. Scanning electron microscopy (SEM) revealed that the ($CuNb_2O_6$) thin films consist of nanoparticles with diameters ranging from 50 to 200 nm, demonstrating homogeneity. The Tauc plot analysis suggested indirect and direct band gaps of approximately 1.94 eV and 1.41 eV, respectively, indicating potential for visible-light absorption as metal oxide photoelectrode materials. When subjected to visible light, the photocurrent density of the ($CuNb_2O_6$) cathode showed a rapid increase, reaching 0.25 mA/cm² at 0.4 V *vs*. RHE in aqueous solutions.

Mohmed et al (2024) conducted a study on the photocatalytic activity of titanium dioxide nanoparticles (TiO_2NPs) for hydrogen evolution reaction (HER), focusing on oxygen-doping with γ-ray irradiation treatment, methanolic dispersion, and post-annealing temperatures. Their results indicated that exposure to high-energy radiation, ranging from 10 kGy to 100 kGy, led to a significant increase in crystallite size, with sizes ranging from 54.22 nm to 55.32 nm, resulting in higher crystallinity. Additionally, post-irradiation conditions caused a reduction in the energy band gap, from 3.25 eV to 3.18 eV, promoting light absorption. Notably, at 70 kGy, there is increasing photocurrent density by over 300% to approximately 100.12 μA/cm² at 1.23 V *vs*. RHE, compared to 36.42 μA/cm² for pure TiO_2NP.

Li et al (2024) have explored the surface manipulation of metal oxide-based photoelectrodes with

overlaid co-catalysts to enhance photoelectrochemical (PEC) water splitting activities. To achieve this, they synthesized nanoparticulated WO_3 films on fluorine-doped tin oxide (FTO) coated glass substrates using a simple sol-gel method. Subsequently, they decorated the photoanode surface with a conformal layer of a QNi complex through drop-coating at ambient temperature. The resulting layer had a thickness of approximately 2 μm. Scanning transmission electron microscopy (STEM) images of the QNi/ WO_3 hybrid structure clearly illustrated the presence of Ni-SAs uniformly distributed on the surface of WO_3 nanospheres. There was enhanced photocurrent density of 2.77 mA/cm² at 1.23 V *vs.* RHE in a 0.1 M KPi electrolyte (pH 7) under 1 sun illumination compared to that of pristine WO_3, which achieved a photocurrent density of 1.01 mA/cm².

Reddy et al (2024) investigated the integration of ZnO with lower bandgap semiconductor nanostructures and carbon nanofibers (CNFs) to improve charge transfer and reduce recombination rates. In this, twisted leaf-like ZnO, flake-like BiOI, ZnO-BiOI nanostructure heterojunctions, and ZnO-BiOI@C composites were synthesized via a solvothermal method. Raman spectroscopy of ZnO revealed peaks attributed to the second-order Raman process, characteristic of Wurtzite ZnO. The bandgaps for these materials were determined to be 3.2 eV for ZnO, 2.0 eV for BiOI, 1.9 eV for ZnO-BiOI, and 1.7 eV for ZnO-BiOI@C, respectively. highlight the superiority of PEC performance (i.e 5.6 mA/cm² under light illumination) of the ZnO-BiOI@C composite.

Meng et al (2024) have worked on constructing a heterojunction and successfully loaded Ag_2O onto Nb_2O_5 photoanode by ion precipitation to effectively enhance the carrier separation efficiency and broaden its photo-response range. The crystal structure of the sample, was confirmed through XRD analysis and using JCPDS standard database. The photo electrode films prepared were used as working electrodes along with platinum and Ag/AgCl as counter and reference electrodes (using 0.5 M Na_2SO_4 aqueous solution as the electrolyte, pH = 6.9). The composite photoanode (NA-3) exhibited an excellent photocurrent density value (0.481 mA/cm^2), which was 2.88 times higher than that of the original electrode, and achieved a negative shift of the onset potential from 0.366 VRHE to 0.227 VRHE. This was attributed to the fact that the holes originally migrating to the surface defect state can be rapidly trapped and allowed to participate in the oxidation reaction.

Qian et al. (2024) investigated the fabrication of TiO_2 nanorods/nanoflower homojunction

photoanodes and further enhanced the oxygen evolution kinetics by incorporating $CoNi_2S_4$ as an oxygen evolution cocatalyst supported on these photoanodes. The microstructure analysis revealed that the TR (TiO_2 nanorods) and the TRF (TiO_2 nanorods/nanoflower) diameters ranging from 100 to 200 nm and 200 nm, respectively, enhanced carrier migration ability. X-ray diffraction patterns confirmed the presence of rutile phase TiO_2 in TR, TF, and TRF photoanodes. The TRF photoanode exhibited a significantly higher current density (1.20 mA/cm^2) compared to TF (0.16 mA/cm^2) and TR (0.7 mA/cm^2) photoanodes at 1.23V *vs.* RHE. This enhanced performance was attributed to the ordered arrangement of rod structures in the TR photoanode, facilitating the migration of photogenerated carriers.

Shinde et al (2024) incorporated Au plasmons in the ZnO/CuO heterojunction to further enhance its optical absorption and facilitate charge carrier transport at the interface through the surface plasmon resonance (SPR) effect. X-ray diffraction analysis revealed the crystal planes of ZnO and CuO, indicating the wurtzite hexagonal structure of ZnO and the monoclinic structure of CuO. The presence of Au plasmons was confirmed by additional diffraction peaks associated with Au crystal planes. In the absorption spectra, the loading of Au plasmons enhanced optical absorption in the visible region, with a characteristic plasmon resonance peak observed at approximately 530 nm. The optical band gap values of thin films, fell in the range of 3.0-3.21 eV.

Mohamed et al (2024) investigated and reported a novel approach to create a highly efficient g-C_3N_4/ThO_2@$BiVO_4$ photoanode through a two-step process involving methanolic dispersion spin-coating followed by electrodeposition (ED). The deposited g-C_3N_4/ThO_2@$BiVO_4$ photoelectrode exhibited a distinctive dual-nanostructure morphology characterized by ‘spongy’ and ‘needle-like’ nanoflower architecture, ultimately forming a densely packed agglomerate. The incorporation of oxygen and approximately 5.8% Th^{4+} doping induced notable photostability. Specifically, the g-C_3N_4/ThO_2@$BiVO_4$ photoanode achieved a significantly enhanced photocurrent density of 0.45 mA/cm^2 at 1.23 V vs. RHE.

Li et al (2024) investigated, WO_3/$CuWO_4$/CuO ternary heterojunction film on FTO substrates for the first time using an in-situ technique, aiming to create an effective photoanode for photoelectrochemical hydrogen production. The incorporation of CuO nanoparticles onto WO_3

nanorods, with a buffer layer of $CuWO_4$, significantly enhanced the absorption capability of visible light, accelerated charge separation, and improved photoelectrochemical performance. Cross-sectional scanning electron microscopy (SEM) images showed that the composite film maintained a vertical structure array, with the nanorod array height approximately 4.26 μm. Further, analysis of the absorption edge of the WO_3/ $CuWO_4$/CuO ternary heterostructure revealed a significant red shift and the strongest light absorption intensity, which was attributed to the characteristic absorption of CuO nanocrystals. The photocurrent density achieved by the WO_3/ $CuWO_4$/CuO heterojunction photoelectrode was 5.6 times higher than that of the bare WO_3 photoanode i.e 2.24 mA/cm^2 at 1.23 V vs. RHE.

Shaheen et al (2023) worked on g-CN supported carbon coated Lanthanum doped tungsten oxide (C@LWO/gCN) composite, synthesized via hydrothermal approach. The photodegradation of different cationic dyes like malachite green (MG), crystal violet (CV) and methylene blue (MB) was investigated under prepared C@LWO/ gCN composite. Furthermore, the comparative photodegradation was also performed using pristine LWO and C@LWO nanowires. The results proved that incorporation of La ions into WO_3 lattice and reduced band gap of doped sample significantly boost up the capability of the material towards photodegradation. The maximum degradation was found out at pH = 6, 5 mg catalyst dose, 5 ppm dye concentration and 35 degree Celsius temperature. The achieved results proved that the trapping agents compete with prepared composite specie for the h^+, e^-, $HO^\bullet$ and $O_2^{\bullet-}$ radicals.

Zhang et al (2023) synthesised Bi_2WO_6 using surfactant assistance strategy, which possesses superior photocatalytic activity under natural environment with outdoor sunlight as illumination source. Rod-like and sheet-like WO_3 were synthesized by controlling rich and poor Cl^- contents in precursor solutions, respectively, which were utilized to construct Bi_2WO_6/WO_3 heterojunctions. Compared with pristine samples, Bi_2WO_6/WO_3 exhibited enhanced tetracycline photodegradation performance under natural environment and the degradation efficiencies reached 74.3% and 54.2% within 150 min on sunny and overcast days, respectively. Moreover, Bi_2WO_6/WO_3 exhibited the effective photodegradation performances toward methyl orange and rhodamine b, with elimination efficiencies of 63.7% and 99.0% within 50 min irradiation, respectively.

Hao et al (2020) prepared the 2D plate-like $WO_3/CuWO_4$ uniform core-shell heterojunction through in-situ synthesis method. After modification with the amorphous Co-Pi co-catalyst, the ternary uniform core-shell structure photoanode achieved a photocurrent of 1.4 mA/cm^2 at 1.23 V *vs.* RHE, which was about 6.67 and 1.75 times higher than that of pristine WO_3 and 2D uniform core-shell heterojunction, respectively. Furthermore, the onset potential of 2D $WO_3/CuWO_4$/Co-Pi core-shell heterojunction was observed with a negatively shifts of about 20 mV. The work provideed a strategy of maximizing the advantages of core-shell heterojunction and co-catalyst to achieve effective PEC performance.

Cui et al (2019) synthesized $ZnWO_4$ - decorated WO_3 nanorod arrays with type II heterojunction structures by a two-step solvothermal method. Characterization confirmed the presence of abundant W^{5+} species in the defected $ZnWO_4$-decorated WO_3 samples, leading to enhanced light absorption and charge-separation efficiency. The decorated WO_3 nanorod arrays showed much higher photoelectrochemical (PEC) activity for water splitting than pure WO_3 nanorod arrays. Specifically, the sample with optimal $ZnWO_4$ decoration and surface defects exhibited a current density of 1.87 mA /cm^2 at 1.23 V *vs.* RHE. However, the decoration of WO_3 with too much $ZnWO_4$ blocked the light absorption of WO_3, inhibiting the PEC performance, even when many defects were present.

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